PATENT SPECIFICATION

(11) 1330947

NO DRAWINGS

1330947

(21) Application No. 23580/71 (22) Filed 19 April 1971

(31) Convention Application No. 17976 (32) Filed 9 March 1970 in

(33) United States of America (US)

(44) Complete Specification published 19 Sept. 1973

(51) International Classification C08G 43/02 C08D 9/10//C08F 33/08

(52) Index at acceptance

C3R 36C15 36C8P 36C8R 36L2C1 36L3A 36L5X 36L6F 36T1

C3P 12C 12D1 2C13A 2C13B 2C13C 2C14B 2C6B 2H4 2H6 2HY 2S2 7C11 7C13A 7C13B 7C13C 7C14B 7C6B 7S2

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(54) PROCESS FOR RUBBER MODIFIED POLYPHENYLENE ETHER

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing a rubber modified polyphenylene ether composition.

The polyphenylene ethers are known and described in numerous publications including U.S. Patents Nos. 3,306,874 and 3,306,875 of Allan S. Hay and U.S. Patents Nos. 3,257,357 and 3,257,358 of Gelu Stoeff Stamatoff. The high molecular weight polyphenylene ethers are high performance engineering thermoplastics possessing relatively high melt viscosities and softening points, i.e., in excess of 275°C, and are useful for many commercial applications requiring high temperature resistance including formation of film, fiber and molded articles.

While possessing the above described desirable properties, it is also known that certain of the properties of the polyphenylene ethers are undesirable for some commercial use. For example, parts molded from polyphenylene ethers are somewhat brittle due to poor impact strength. In addition, the relatively high melt viscosities and softening points are considered a disadvantage for many uses. Film and fiber can be formed from a phenylene ether on a commercial scale using solution techniques, but melt processing is commercially unattractive because of the required high temperatures needed to soften the polymer and the problem associated therewith such as instability, discoloration and a requirement for specially designed process equipment to operate at elevated temperatures. Molded articles can be formed by melt processing techniques, but again, the high temperatures required are undesirable.

It is known in the art that the properties of the polyphenylene ethers can be materially altered by blending with other polymers. For example, one method for improving the melt-processability of the polyphenylene ethers is disclosed in U.S. Patent No. 3,379,792. According to this patent, flow properties of the polyphenylene ethers are improved by blending with from about 0.1 to 25 parts by weight of a polyamide. In U.S. Patent No. 3,361,851, a polyphenylene ether composition comprising a polyphenylene ether blended with a polyolefin is disclosed. The polyolefin is added to improve impact strength and resistance to aggressive solvents. In U.S. Patent No. 3,383,435, there is provided a means for simultaneously improving the melt processability of the polyphenylene ethers while simultaneously up-grading many properties of polystyrene. The invention of this patent is based upon the discovery that the polyphenylene ethers and polystyrenes, including the modified polystyrenes, are combinable in all proportions resulting in blends having many properties improved over those of either of the components.

A preferred embodiment of U.S. Patent No. 3,383,435, is a composition comprising a high-impact, rubber reinforced polystyrene and a poly - (2,6 - dialkyl - 1,4 - phenylene)-ether. This composition is preferred because it obtains the aforementioned objectives of improving the melt processability of the polyphenylene ether and provides the further

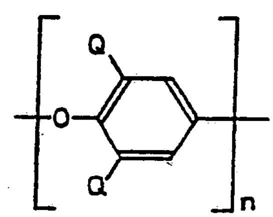
advantage of improving impact resistance of parts molded from the blend. Further, the blend of the polyphenylene ether and the high impact polystyrene may be custom formulated to provide predetermined properties ranging between those of the polystyrene and those of the polyphenylene ether by controlling the ratio of the two polymers. The reason for this is that the blend exhibits a single set of thermodynamic properties rather than two distinct sets of properties—i.e., one for each of the components of the blend as is typical with blends of the prior art.

It has been found that the impact resistance of the polyphenylene ether is improved due to the polybutadiene or rubber content of the high-impact polystyrene and in this respect, it has been additionally found that the improvement in impact strength is directly proportional to the rubber content of the polystyrene. Since high impact strength is a desirable property of a molded part, an obvious method for improving impact strength further might appear to be to blend the polyphenylene ether with a rubber-modified polystyrene having a higher polybutadiene content. However, as a practical limitation, commercially available rubber-modified polystyrenes do not have as high a polybutadiene content as might be desired for this purpose. Another seemingly obvious method for increasing the rubber content would be to add polybutadiene to a powder blend of the polystyrene and the polyphenylene ether prior to forming, such as by extrusion into pellets. However, it has been found that due to the rubbery nature of the polybutadiene, the particles of polybutadiene tend to coalesce or aggregate during the forming operation resulting in relatively large aggregrates or nodules of polybutadiene contained in the molded part. As a result, various of the physical properties of the molded part are impaired. To avoid this problem, very small particles of polybutadiene have been prepared by freezing larger, commercially available particles and grinding the frozen particles prior to blending with the polyphenylene ether and polystyrene. This is an apparently impractical method for preparing blends.

In our co-pending Application No. 21419/71 (Serial No. 1330586) there is disclosed a process for increasing rubber content in a polyphenylene ether while avoiding the problems noted above. The process comprises polymerizing a monomeric phenol to a normally solid polyphenylene ether in a liquid reaction medium containing dissolved rubber, and recovering polymeric components from the reaction mixture in the form of a precipitate by adding a non-solvent precipitant. After drying, the recovered precipitate comprises a free flowing powder consisting of the polyphenylene ether and the rubber, which powder is suitable for molding operations such as by extrusion, cold forming and the like. It is believed that the powder obtained by this co-pending process differs from a simple homogeneous admixture of polyphenylene ether and rubber due a possible grafting or co-reaction between the polyphenylene ether and rubber during the polymerization reaction.

The present invention also seeks to overcome the difficulties noted above and provide a process for increasing the rubber content in a polyphenylene ether composition. Moreover, as in the above-noted copending application, by practice of the present invention, both polybutadiene and other rubbers may be added to a polyphenylene ether, with or without other polymeric additives. The process of the present invention comprises providing a solution of a pre-formed polyphenylene ether and rubber in a solvent medium and recovering the solids from solution by admixture with a non-solvent. The precipitate recovered comprises a finely divided homogeneous admixture of the polyphenylene ether and the rubber suitable for forming into any desired shape such as by compression molding, extrusion or the like. Thus, molded parts formed from powder blends prepared in accordance with the process of this invention, are free of relatively large aggregates of the rubber.

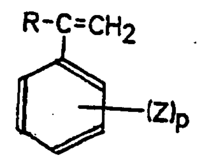
The polyphenylene ethers with which this invention is concerned are preferably those having repeating structural units of the formula:—



where the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 100, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and phenyl nucleus. Examples of polyphenylene ethers corresponding to the above formula can be found in the above-referenced patents of Hay and Stamatoff. The more preferred polyphenylene ethers, for purposes of the present invention, are those having alkyl

substitution in the two positions ortho to the oxygen ether atom—i.e., where each Q is alkyl, most preferably, having from one to four carbon atoms. The most preferred polyphenylene ether for purposes of the present invention is poly - (2,6 - dimethyl - 1,4 - phenylene) ether.

As noted above, the polyphenylene ethers in accordance with the invention may be used alone or in combination with an additional resin, preferably a polystyrene and most preferably a high-impact polystyrene. As disclosed in the above-noted U.S. Patent No. 3,383,435, the styrene resin combineable with the polyphenylene ether is one having at least 25% by weight polymer units derived from a monomer having the formula:



where R is hydrogen, lower alkyl or halogen; Z is a member selected from the class consisting of vinyl, hydrogen, halogen and lower alkyl; and p is 0 or a whole number equal to from 1 to 5. The preferred styrene resin for purposes of this invention is one comprising polystyrene blended with from about 30 to 35% by weight polybutadiene. Lower alkyl is defined in this connection as having from 1 to 4 carbon atoms.

For brevity, the term "polyphenylene ether composition" as used in this description, shall include within its scope, the polyphenylene ethers alone, or as blended with other resins such as the polystyrenes described above. In addition, it should be understood that the term encompasses polyphenylene ethers containing other additives as would be obvious to those skilled in the art such as stabilizers, pigments and plasticizers.

In accordance with the invention, a rubber is added to the preformed polyphenylene ether composition primarily to improve impact strength. Though polybutadiene is the rubber heretofore used in conjunction with the polyphenylene ether (added to the composition in the form of high-impact polystyrene), the present invention makes possible the addition of substantially any rubber with a resulting improvement in impact strength, though polybutadiene still constitutes the most preferred embodiment as it appears to provide the most substantial improvements. Examples of other rubbers within the scope of this invention include modified polybutadiene such as the hydroxy and carboxy terminated polybutadienes, polychlorobutadiene known commercially as the neoprenes, polyisobutylenes including copolymers with isoprene, polyisoprene, copolymers of ethylene and propylene, copolymers of various diolefins and acrylic nitriles, polysulfide rubbers, acrylic rubbers, polyurethanes, copolymers of butadiene or isoprene and various co-monomers such as methyl methacrylate, 3 - 4 - dichloro - α - methyl styrene, methylisopropenyl ketone, vinyl pyridine, styrene and other related unsaturated monomers, polyether rubbers and epichlorohydrin rubbers.

The amount of rubber present in the formulation is not critical to the invention, the improvement in impact strength being substantially directly proportional to the concentration of the rubber. However, dependent upon the particular rubber used, there is a maximum concentration beyond which the particles of the rubber begin to coalesce and form nodules within the molded part, thereby impairing various physical properties. A maximum of 30% by weight rubber is set forth herein for purposes of establishing a guideline, but this may vary dependent upon the rubber used as noted above. Below about 1% rubber, little improvement in impact resistance is obtained and this represents a practical minimum amount for purposes or this invention. A preferred range for the rubber varies from about 5% to 20% by weight of the blend.

Where other resins are used in conjunction with the polyphenylene ethers, such as polystyrenes or rubber-modified high-impact polystyrene, they are used in their customary amounts, but it is preferred when the latter type of resin is used that the polyphenylene ether should be present in an amount less than that of the polystyrene. A most preferred composition in accordance with this invention comprises a polyphenylene ether in an amount from 30 to 50% by weight, a polystyrene in an amount of from 30 to 50% and a rubber in an amount of from 5 to 20%.

As noted above, the blend of polymer and rubber is prepared by providing a solution comprising the polyphenylene ether, other blend components, and rubber in a solvent medium and precipitating the mixture by addition of a common non-solvent precipitant. It should be noted that recovery of a polymer with a non-solvent is not uncommon in the art and such procedures have heretofore been employed for the recovery of a substantially pure polyphenylene ether by precipitation with an alcoholic non-solvent such as methanol from a solution in a solvent such as benzene. The invention herein is the preparation of a blend of the polyphenylene ether and rubber avoiding prior art problems such as nodular formation and the like.

With knowledge of the inventive concept and the polymers contemplated, the selection of suitable solvent and non-solvent combinations should be obvious to one skilled in the

art and suitable solvents and non-solvents can be readily ascertained by reference to standard handbooks and by routine experimentation. In general, the solvent should be a good solvent for the polyphenylene ether though it need only be a fair solvent for the rubber, incomplete dissolution of the rubber being satisfactory. In this respect, the term "solvated rubber" is defined to mean rubber completely or partially dissolved in the solvent medium. Preferred solvents for purposes of this invention are the monocyclic aromatic solvents such as benzene, toluene, xylene and the halogenated forms thereof such as dichlorobenzene. Other good solvents are halogenated aliphatic solvents such as trichloroethylene and perchloroethylene. Good non-solvents for both the polyphenylene ethers and most rubbers generally include alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, n - propyl alcohol, n - butyl alcohol, sec - butyl alcohol and methylisobutyl carbinol; esters such as ethylacetate, isopropylacetate, n - butylacetate, sec - butylacetate, amyl acetate, methylamyl acetate, hexyl acetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, and ethylene glycol monobutyl ether acetate; glycol ethers such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, and diethylene glycol monobutyl ether.

Most preferred solvents are the aromatic solvents, especially the monocyclic hydrocarbon solvents such as benzene and toluene. Most preferred non-solvents are the alcohols, especially the aliphatic alcohols having from 1 to 4 carbon atoms such as methanol and ethanol.

It should be obvious that though the above solvents and non-solvents have been set forth as generally suitable for purposes of illustration, there may be various combinations of polyphenylene ethers and specific rubbers for which one or more of the aforesaid solvents and non-solvents would not be appropriate, and that the choice of a specific solvent or non-solvent would depend upon the specific polymers used.

In carrying out the process of the invention, the concentration of the polyphenylene ether and the rubber in the solvent prior to precipitation is not critical. Generally, they may be contained in solution in an amount up to solubility limits of the particular solvent used. Preferably, a reaction medium containing from about 10 to 30% by weight polymer components is preferred.

The polyphenylene ether and rubber is recovered from solution by admixture with a non-solvent for the materials. This is desirably accomplished by slowly adding the reaction medium containing the polyphenylene ether and rubber to the non-solvent with recovery of the precipitate as it forms. To obtain a uniform powder having a relatively small particle size, the non-solvent is preferably agitated by a high speed stirrer during the addition of the solution to the non-solvent.

Recovery of the precipitate from the non-solvent is in accord with art recognized practices such as by filtration or centrifugation. Following recovery, the powders are dried and may then be molded to any desired shape using standard molding procedures. For example, the powders can be passed through an extruder and chopped into pellets for subsequent molding. Alternatively, the powders can be molded directly to any desired shape. The specific forming procedure used does not constitute a part of this invention. Also, prior to molding, the powder blend can be further blended by mechanical means with an additional polymer such as polystyrene.

Though not wishing to be bound by theory, it is believed that the recovered precipitate differs from that of the above noted co-pending application No. 21419/71 (Serial No. 1330586) in that it comprises a simple mechanical admixture of the polyphenylene ether and rubber while the precipitate of the co-pending application is believed to comprise co-reacted, at least in part, polyphenylene ether and rubber.

The invention is illustrated by the Examples which follow:

Example 1

A solution was prepared comprising 1000 grams of a poly - (2,6 - dimethyl - 1,4 - phenylene) ether identified as PPO polyphenylene ether available from the General Electric Company and 200 grams of polybutadiene sold under the registered Trade Mark "SOLPRENE" 203 by the Phillips Petroleum Company, dissolved in 16 liters of toluene. The so formed solution was slowly added to 21 liters of methanol with high speed mixing as the precipitate formed. The precipitate was recovered from solution and dried. A finely divided homogeneous admixture of powders was obtained. The powders were molded into tensile bars and found to have a heat distortion temperature of 181°C, an Izod impact strength of 6.86 Ft.-lb./in. of notch, a tensile yield of 8,000 psi, a tensile strength of 8900 psi and a percent elongation of 70%.

Example 2

The procedure of Example 1 was repeated, but the solution was prepared from 880 grams of the polyphenylene ether, 200 grams of the p lybutadiene and 920 grams of a crystal polystyrene identified as Dylene 8 available from the Sinclair Copper Company. The

powders were precipitated as a finely divided, homogeneous admixture and molded into test bars. The bars were found to have a heat distortion temperature of 123°C, an Izod impact strength of 3.17 Ft.-lb./in. of notch, a tensile yield of 8700 psi. a tensile strength of 7600 psi and an elongation of 17%.

Example 3

The procedure of Example 1 is repeated substituting benzene as the solvent and isopropanol as the non-solvent. Similar results are obtained.

Examples 4 to 6

The procedure of Example 2 is repeated substituting a styrene-butadiene block copolymer for the polybutadiene. The styrene butadiene block copolymer used was identified as Kraton 4119 of the Shell Chemical Company. The composition of the blends formed and their physical properties are set forth in the following table:

Composition (wt.%)	4	5	6
Polyphenylene ether	80	45	45
Polystyrene	6.5	47	48.5
Styrene-butadiene copolymer	13.5	8	6.5
Physical property			
Heat Distortion Tempt. (°C)	164	126	129
Izod Impact (ft.lb/in. of notch)	5.94	3.06	2.20
Tensile Yield (psi)	9,100	9,800	10,400
Tensile Strength (psi)	9,200	7,900	8,000
Elongation (%)	57	30	40

Example 7

The procedure of Example 1 was repeated using 1700 gm of the polyphenylene ether and 300 gm of the "Solprene" 203. To 530 gm of finely divided, homogeneous powder recovered from solution was added 470 gm of finely divided crystal polystyrene. This blend was extruded and molded into test bars. The bars were found to have a heat distortion temperature of 125°C, an Izod impact of 2.43 ft.-lb./in. of notch, a tensile yield of 10,100 psi, a tensile strength of 7,700 psi, and an elongation of 53%.

Example 8

The procedure of Example 1 was repeated using 800 gm of polyphenylene ether and 400 gm of a mixture of random and block copolymer of butadiene (48%) and styrene (52%) available from Phillips Petroleum Co. as "Solprene" 303. To 600 gm of finely divided powder obtained by precipitation was added 400 gm of finely divided crystal polystyrene. The blend was then extruded and molded into test bars. These bars were found to have a tensile yield strength of 8,600 psi, a tensile strength of 7,400 psi, an Izod impact strength of 3.07-ft.lb. and an elongation of 50%.

Example 9

The procedure of Example 1 was repeated using 900 gm of polyphenylene ether and 133 gm of a 75/25 random copolymer of butadiene and styrene available from Phillips Petroleum Co. as Solprene 1206. To 575 gm of powder obtained by precipitation was added 425 gm of chystal polystyrene. The blend was extruded and molded into test bars. These bars had a tensile yield strength of 10,400 psi, a tensile strength of 7,900 psi, an elongation of 28% and an Izod impact strength of 1.86 ft.-lb./inch of notch.

Example 10

The procedure of Example 1 was repeated using 1200 gm of polyphenylene ether and 180 gm of a butadiene-styrene block copolymer containing 75% butadiene and available commercially as "Solprene" 1205 from the Phillips Petroleum Co. To 625 gm of the rubber modified polyphenylene ether was added 475 gm of crystal polystyrene. This blend was extruded and molded into test bars. The bars had a heat distortion temperature of 125°C, an Izod impact of 1.5 ft.-lb., a tensile yield of 11,200 psi, a tensile strength of 8,700 psi and an elongation of 39%.

Example 11

The procedure in Example 10 was repeated using 700 gm of polyphenylene ether and 208 gm of "Solprene" 1205. A blend was prepared from 648 gm of this rubber modified polyphenylene ether and 352 gm of crystal polystyrene, extruded and molded into test bars. These bars had an izod impact of 4,45 ft.-lb./inch of notch, a tensile yield of 9,700 psi, a tensile strength of 8,600 psi, and an elongation of 73%.

Example 12

A solution of 800 gm of polyphenylene ether in toluene was prepared and precipitated as in Example 10. The fine powder was extruded and molded into test bars. These bars were found to have a heat distortion point of 192°C, an Izod impact of 1.2 ft.-

lb./inch of notch, a tensile yield of 11,600 psi, a tensile strength of 9,200 psi, and an elongation of 48%.

Example 13

The procedure in Example 2 was repeated using 450 gm of polyphenylene ether and 550 gm of crystal polystyrene. Molded bars made from this material had a heat distortion point of 124°C, a tensile yield of 12,000 psi, a tensile strength of 5,500 psi, an Izod impact of 0.46 ft.lb./inch of notch, and an elongation of 13%.

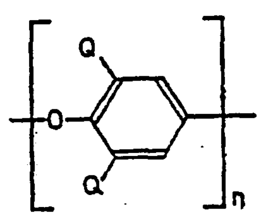
Example 14

The procedure of Example 2 was repeated using 450 gm of polyphenylene ether and 550 gm of high impact polystyrene identified as Cosden 825-TV from the Cosden Oil Co. Molded bars had a heat distortion temperature of 123°C, an Izod impact of 2.60 ft.-lb./inch of notch, a tensile yield of 10,000 psi, a tensile strength of 8,300 psi, and 33% elongation.

WHAT WE CLAIM IS:—

1. A process for preparing a powder composition comprising a polyphenylene ether and a rubber, comprising the steps of dissolving a polyphenylene ether and solvating a rubber in a solvent medium to form a solution of said polyphenylene ether and solvated rubber (as herein defined), and precipitating said polyphenylene ether and rubber as a homogeneous mixture of finely divided powders by admixture of said solution with a non-solvent for said polyphenylene ether and said rubber.

2. A process according to Claim 1, wherein said polyphenylene ether corresponds to the formula:



wherein n is a positive integer and is at least 100, and each Q represents hydrogen, halogen, a hydrogen radical, a halohydrocarbon radical having at least two carbon atoms between the halogen atom and the phenyl nucleus, a hydrocarbonoxy radical, or a halohydrocarbonoxy radical having at least two carbon atoms between the halogen atom and the phenyl nucleus.

3. A process according to Claim 2 wherein said polyphenylene ether is a poly - (2,6 - dimethyl - 1,4 - phenylene) ether.

4. A process according to any preceding Claim, wherein the polyphenylene ether is dissolved in the solvent in an amount in excess of the rubber.

5. A process according to any preceding Claim, wherein said rubber is a polybutadiene, an hydroxy-terminated polybutadiene, a carboxy-terminated polybutadiene, a polychlorobutadiene, a polyisobutylene, a copolymer of isobutylene with isoprene, a polyisoprene, a copolymer of ethylene with propylene, a copolymer of a diolefin with an acrylic nitrile, a polysulfide rubber, an acrylic rubber, a polyurethane rubber, a copolymer of butadiene or isoprene with methylmethacrylate, 3,4 - dichloro - α - methyl styrene, methylisopropenyl ketone, vinyl pyridine or styrene, a polyether rubber or an epichlorohydrin rubber.

6. A process according to Claim 5, wherein said rubber is a polybutadiene.

7. A process according to any preceding Claim, wherein said rubber is present in said mixture in an amount of from 1% to 30% by weight of total solids.

8. A process according to Claim 7, wherein said rubber is present in said mixture in an amount of from 5% to 20% by weight of total solids.

9. A process according to any preceding Claim, wherein said solvent is an aromatic monocyclic hydrocarbon or a halogenated hydrocarbon.

10. A process according to Claim 9, wherein said solvent is benzene or toluene.

11. A process according to any preceding Claim, wherein said non-solvent is an alcohol, ester or glycol ether.

12. A process according to Claim 11 wherein said non-solvent is a (C_1—C_6) alkyl alcohol.

13. A process according to Claim 12, wherein said non-solvent is methanol.

14. A process according to any preceding Claim, wherein a polystyrene is also dissolved in said solution prior to precipitation with said non-solvent.

15. A process according to Claim 14, wherein the polystyrene is a rubber modified high impact polystyrene.

16. A process according to Claim 15, wherein the polyphenylene ether is dissolved in the solvent in an amount less than that of the rubber modified polystyrene.

17. A process according to any preceding Claim, wherein said finely divided powders of polyphenylene ether and rubber are subsequently blended with a polystyrene.

18. A process according to Claim 17, wherein said polystyrene is a rubber modified polystyrene.

19. A process according to any one of Claims 14—18, wherein said mixture comprises 30% to 50% by weight polyphenylene ether, 30% to 50% by weight polystyrene,

and 5% to 20% by weight rubber, based on the weight of total solids.

20. A process for preparing a powder composition comprising a poly - (2,6 - dimethyl - 1,4 - phenylene) ether and a polybutadiene, which comprises dissolving a major portion of a poly - (2,6 - dimethyl - 1,4 - phenylene) ether and solvating 1% to 30% by weight of a polybutadiene in a monocyclic aromatic solvent to form a solution of said poly - (2,6 - dimethyl 1,4 - phenylene) ether and solvated polybutadiene (as herein defined), and precipitating said poly - (2,6 - dimethyl - 1,4 - phenylene) ether and polybutadiene as a homogeneous mixture of finely divided powders by admixture of said solution with a lower alkyl alcohol containing up to 6 carbon atoms.

21. A process for preparing a powder composition, according to Claim 1 and substantially as described in any one of the Examples herein.

22. A powder composition comprising a polyphenylene ether and a rubber, whenever obtained by a process according to any preceding Claim.

23. A shaped article formed by molding a composition according to Claim 22.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.